Code: 846-68536
Ref.: Johnson, N

JAPANESE PATENT OFFICE

PATENT JOURNAL

KOKAI PATENT APPLICATION NO. HEI 6[1994]-271506

Technical Disclosure Section

Int.Cl.[5]:	C 07 C 69/96 B 01 J 27/08 27/138 31/04 C 07 C 68/00 // C 07 B 61/00
Sequence Nos. for Office Use:	9279-4H 9342-4G 9342-4G 9279-4H
Application No.:	Hei 5[1993]-56860
Application Date:	March 17, 1993
Publication Date:	September 27, 1994
Number of Claims:	3 (total of 5 pages; OL)
Examination Request:	Not requested

MANUFACTURE OF AROMATIC CARBONATE ESTERS

Inventor:

Hiroshi Iwane
Mitsubishi Chemical Corp.
Tsuba Research Laboratory
8-3-1 Chuo-ku, Ami-machi,
Inashiki-gun, Ibaraki-ken

Takahiro Komeyama
Mitsubishi Chemical Corp.
Tsuba Research Laboratory
8-3-1 Chuo-ku, Ami-machi,
Inashiki-gun, Ibaraki-ken

Hidekazu Miyagi
Mitsubishi Chemical Corp.
Tsuba Research Laboratory
8-3-1 Chuo-ku, Ami-machi,
Inashiki-gun, Ibaraki-ken

Applicant:

000006057
Mitsubishi Chemical Corp.
2-5-2 Marunouchi,
Chiyoda-ku, Tokyo

Agent:

Takaya Yamamoto, patent attorney

[There are no amendments to this patent.]

Abstract

Constitution

A method for manufacturing aromatic carbonate esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, where said reaction is carried out in a reaction

system in the presence of (A) one or more substances selected from palladium and palladium compounds, (B) a manganese compound, (C) a cobalt compound, and (D) one or more inorganic halides selected from alkali metal halides and alkaline earth metal halides.

Effect

An industrial manufacturing method for aromatic carbonate esters is offered that allows for the efficient manufacture of aromatic carbonate esters while maintaining high catalytic activity.

Claims

1. A method for manufacturing aromatic carbonate esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, said method for manufacturing aromatic carbonate esters being characterized in that said reaction is carried out in a reaction system in the presence of (A) one or more substances selected from palladium and palladium compounds, (B) a manganese compound, (C) a cobalt compound, and (D) one or more inorganic halides selected from alkali metal halides and alkaline earth metal halides.

2. The method according to Claim 1, wherein the inorganic halide is a substance selected from chloride and bromide.

3. The method according to Claim 2, wherein the inorganic halide is a substance selected from cesium chloride, sodium bromide, potassium bromide, rubidium bromide, cesium bromide and barium bromide.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention concerns a method for the manufacture of aromatic carbonate esters using a special catalyst. Aromatic carbonate esters, particularly diphenyl carbonate, are useful as raw materials in the production of polycarbonate and other substances.

[0002]

Prior art

In the past, methods wherein an aromatic hydroxy compound and phosgene are allowed to react have been used for manufacturing aromatic carbonate esters. However, these methods are undesirable due to the high toxicity of phosgene. Thus, a number of methods have been offered that do not use phosgene whereby aromatic carbonate esters are manufactured in a reaction between an aromatic hydroxy compound, carbon monoxide and oxygen.

[0003]

With regard to catalysts that are used in such methods, a method is described in Japanese Kokoku Patent No. Sho 56[1981]-38144 wherein a palladium compound, a compound

containing a metal from group IIIA, IVA, VA, VIA, IB, IIB, VIB or VIIB of the periodic table and a base are used; a method is described in Japanese Kokoku Patent No. Sho 56[1981]-38145 wherein a palladium compound, manganese complex, cobalt complex, base and desiccant are used; a method is described in Japanese Kokai Patent Application No. Hei 1[1989]-165551 wherein a palladium compound, iodine compound and zeolites are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-104564 wherein a palladium compound, divalent or trivalent manganese compound, tetraalkylammonium halide and quinones are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-142754 wherein a palladium compound, cobalt compound, tetraalkylammonium halide and quinones are used; a method is described in U.S. Patent No. 5,142,086 wherein a catalyst comprising a metal auxiliary catalyst selected from a palladium compound, quaternary ammonium salt, cobalt, iron, cerium, manganese, molybdenum, samarium, vanadium, chrome and copper, and an organic auxiliary catalyst selected from an aromatic ketone, aliphatic ketone or aromatic polycyclic hydrocarbon is used; and a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-25095 wherein palladium or a palladium compound, cobalt compound, halide and basic compound are used.

[0004]

In addition, examples of methods that are used in order to prevent the hydrolysis of the aromatic carbonate esters due to water that is generated in the reaction include a method wherein a large quantity of desiccant is used simultaneously (Japanese

Kokai Patent Application No. Sho 54[1979]-135744) and a method wherein water is removed by distillation of the reactants (Japanese Kokai Patent Application No. Hei 4[1992]-261142). To describe catalyst systems that have been offered in the past in general terms, the systems can generally be conceived as being three-component systems consisting of palladium catalyst + auxiliary catalyst + additive. In the reaction between the aromatic hydroxy compound, carbon monoxide and oxygen, aromatic carbonate ester is generated by the palladium catalyst under acidic conditions, the auxiliary catalyst re-oxidizes the palladium catalyst after the reaction, and the additives are used in order to accelerate said reaction. Manganese compounds or cobalt compounds are particularly useful as auxiliary catalysts, and compounds containing bromide ions are particularly useful as additives. In addition, the use of hydroquinone and other organic auxiliary catalysts or amines and other bases also appears to be effective.

[0005]

Problems to be solved by the invention

The inventors of the present invention et al. carried out addition tests and other investigations of conventional technology using phenol as a substrate, and discovered the following problems with conventional catalysts.

(i) Although the reaction progresses at a sufficiently high rate initially when a manganese compound is used as an auxiliary catalyst, the reaction stops mid-way, and moreover, hydrolysis of

the esters that are produced progresses due to the water that is co-produced.

(ii) The reaction is generally slow when a cobalt compound is used as a catalyst.

The present invention solves these problems with the aforementioned conventional catalyst systems, and offers a method for industrial manufacture of aromatic carbonate esters whereby efficient manufacture of carbonate esters is possible while maintaining high catalytic activity.

[0006]

Means to solve the problems

The present invention was perfected when the inventors of the present invention discovered that the rate of production of aromatic carbonate esters is increased by using the specific catalyst systems described below. Specifically, the present invention is a method for manufacturing aromatic carbonate esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, said method for manufacturing aromatic carbonate esters being characterized in that said reaction is carried out in a reaction system in the presence of (A) one or more substances selected from palladium and palladium compounds, (B) a manganese compound, (C) a cobalt compound, and (D) one or more inorganic halides selected from alkali metal halides and alkaline earth metal halides.

[0007]

The inventors of the present invention et al., as a result of investigations concerning conventional technology using phenol as a substrate, discovered that mid-way stoppage of the reaction, and hydrolysis of the ester product that occur when a manganese compound is used as an auxiliary catalyst, are caused by side-reactions whereby the bromide ions in the additives are depleted as phenol is converted to bromophenol via bromination. The present invention thus provides an industrial method for manufacturing aromatic carbonate esters where the side-production of bromophenol is controlled due to the synergistic action of manganese compounds and cobalt compounds.

[0008]

1. Reaction raw materials

(1) Aromatic hydroxy compound

The aromatic hydroxy compound that is used in the present invention is an aromatic mono- or polyhydroxy compound. Examples include phenol; p-cresol, xylenol, trimethylphenol, tetramethylphenol, ethylphenol, propylphenol, methoxyphenol, ethoxyphenol, chlorophenol, dichlorophenol, bromophenol, dibromophenol and other substituted phenols and isomers thereof; naphthol, methylnaphthol, ethylnaphthol, chloronaphthol, bromonaphthol and other substituted naphthols and isomers thereof; 2,2-bis(4-hydroxyphenyl)propane and various other bisphenols; various biphenols; various hetero-aromatic hydroxy

compounds and stereoisomers thereof; as well as compounds produced by the substitution of alkyl groups or halogen atoms thereupon. Of these compounds, phenol is particularly desirable.

[0009]

(2) Carbon monoxide

The carbon monoxide that is used in the present invention can be a gas that is produced by starting with a high-purity substance and diluting it with another gas that does not have a detrimental influence on the reaction, such as nitrogen, argon or carbon dioxide.

(3) Oxygen

The oxygen that is used in the present invention can be a gas that is produced by starting with a high-purity substance and diluting it with another gas that does not have a detrimental influence on the reaction, such as air, nitrogen, argon or carbon dioxide.

[0010]

2. Catalyst

The catalyst that is used in the present invention contains the four components (A)-(D) below.

(A) Palladium and palladium compounds

The palladium and palladium compounds that are used in the present invention are palladium black, palladium carbon, palladium/alumina, palladium/silica or other palladium/carrier combinations; palladium chloride, palladium bromide, palladium iodide, palladium sulfate, palladium nitrate or other inorganic palladium salts; and palladium acetate, palladium oxalate or other organic palladium acid salts. In addition, substances that can also be used include palladium (II) acetylacetonate, palladium complexes produced by the coordination of carbon monoxide, nitriles, amines, phosphines or olefins with palladium, examples of which include $PdCl_2(PhCN)_2$, $PdCl_2(PPh_3)_2$, $Pd(CO)(PPh_3)_3$, $(Pd(NH_3)_4)Cl_2$, and $Pd(C_2H_4)(PPh_3)_2$, or mixtures of palladium with compounds generated by these complexes in the reaction system. The amount of palladium component that is used in the reaction is preferably in the range of 10^{-5} to 1in terms of the mole ratio with respect to the aromatic hydroxy compound, with a range of 10^{-4} to 10^{-1} being particularly desirable.

[0011]

(B) Manganese compound

The manganese compound that is used in the present invention is preferably a divalent or trivalent manganese compound, examples of which include manganese fluoride, manganese chloride, manganese bromide, manganese iodide, manganese sulfate, manganese carbonate, manganese nitrate and other inorganic salts; manganese formate, manganese acetate, manganese benzoate and other organic

acid salts; manganese (II) or (III) acetylacetonate, complexes produced by the coordination of carbon monoxide, nitriles, amines, phosphines or olefins with manganese; and mixtures of manganese salts and compounds formed in the reaction system by these complexes. There are no particular restrictions on the amount of manganese component that is used in the reaction, but a molar ratio in the range of 10^{-3} to 10^{2} with respect to the palladium component (A) is preferred, with a range of 10^{-2} to 10 being particularly desirable.

[0012]

(C) Cobalt compound

Examples of cobalt compounds that are used in the present invention are preferably divalent or trivalent cobalt compounds, such as cobalt fluoride, cobalt chloride, cobalt bromide, cobalt iodide, cobalt sulfate, cobalt carbonate, cobalt nitrate, cobalt hydroxide and other inorganic salts, cobalt formate, cobalt acetate and other organic acid salts; cobalt (II) or (III) acetylacetonate or complexes wherein carbon monoxide, nitriles, amines, phosphines or olefins are coordinated with cobalt; and mixtures of cobalt and compounds that are generated in the reaction system by these complexes. The amount of cobalt compound that is used in the reaction has no particular restrictions, but a molar ratio in the range of 10^{-4} to 10^{2} with respect to the palladium component (A) is preferred, with a range of 10^{-3} to 10 being particularly desirable.

[0013]

(D) Inorganic halide

Alkali metal or alkaline earth metal halides are used as the inorganic halide in the method of the present invention. Examples of preferred halides include chlorides and bromides, with cesium chloride, sodium bromide, potassium bromide, rubidium bromide, cesium bromide and barium bromide being preferred. There are no particular restrictions on the amount of inorganic halide that is used in the present invention, but a mole ratio in the range of 10^{-2} to 10^{3} with respect to the palladium component (A) is preferred, with a range of 10^{-1} to 10^{2} being particularly desirable.

[0014]

3. Reaction conditions

The reaction is performed by introducing the aforementioned aromatic hydroxy compound and the aforementioned components (A)-(D) into the reaction apparatus, pressurizing the system with carbon monoxide and oxygen, and then carrying out the reaction while stirring and heating. The reaction pressure is 0.1-500 atm total pressure, with a range of 1-250 atm being preferred. It is preferable, from the standpoint of safety, for the compositional ratio of carbon monoxide and oxygen to be far from the combustion range. The reaction temperature is in the range of 20-300°C, with 60-250°C being preferred, and 100-200°C being additionally desirable. Examples of solvent that can be used in the reaction

include hexane, heptane, cyclohexane, benzene, toluene, xylene, methylene chloride, chloroform, chlorobenzene, diethyl ether, diphenyl ether, tetrahydrofuran, dioxane, ethyl acetate, methyl formate, acetonitrile and other inert solvents. There are cases where the raw material aromatic hydroxy compound serves as the reaction solvent, and it is not particularly necessary to use another solvent in such cases.

[0015]

Application examples

The present invention is described in detail below by providing application examples and comparative examples.

Application Example 1

3.63 g (39 mmol) of phenol, 21.2 mg (10 μg atoms) of 5% palladium/carbon, 2.4 mg (10 μmol) of manganese (II) acetate tetrahydrate, 2.5 mg (10 μmol) of cobalt (II) acetate tetrahydrate and 128 mg (0.60 mmol) of cesium bromide were introduced into a Hastelloy autoclave with an inner volume of 30 mL. After replacing the interior of the system with carbon monoxide, carbon monoxide was introduced at 60 atm, dry air was introduced at 30 atm, and the reactants were mixed by stirring for 3 h at 100°C using a stir bar. After completion of the reaction, the reaction solution was quantitatively analyzed by gas chromatography. The results indicated a diphenyl carbonate yield of 5.6% (1.1 mmol). By-products of o- and p-bromophenol were not seen.

[0016]

Application Examples 2-6

A reaction was carried out in the same manner as in Application Example 1, with the exception that the halides shown in Table I were used in the amounts shown in Table I (0.60 mmol for each) instead of the 128 mg (0.60 mmol) of cesium bromide. The yields of the resulting diphenyl carbonates are shown in Table I. No by-products of o- and p-bromophenol were seen in any of the examples.

[0017]

Table I

//insert table I, p. 4//

Key: 1 Application Example
2 Halide
3 Diphenyl carbonate yield

[0018]

Comparative Example 1

A reaction was carried out in the same manner as in Application Example 1, with the exception that cesium bromide was not used. The diphenyl carbonate yield was 0.55% (0.11 mmol).

[0019]

Comparative Example 2

A reaction was carried out in the same manner as in Application Example 1, with the exception that cobalt (II) acetate tetrahydrate was not used. The diphenyl carbonate yield was 5.4% (1.0 mmol), but o- and p-bromophenol were produced as by-products at a total of 31% (0.19 mmol) with respect to the bromide that was used.

[0020]

Comparative Example 3

A reaction was carried out in the same manner as in Application Examples 1 and 2, but manganese (II) acetate

tetrahydrate was not used. Although the by-products o- and p-bromophenol were not seen, the yield of diphenyl carbonate was 1.6% (0.31 mmol).

[0021]

Application Example 7

A reaction was carried out in the same manner as in Application Example 1, with the exception that 2.2 mg (10 μmol) of palladium (II) acetate was used instead of 5% palladium/carbon. Diphenyl carbonate was obtained at a yield of 5.0%, and the by-products o- and p-bromophenol were not seen.

[0022]

Application Example 8

A reaction was carried out in the same manner as in Application Example 1, with the exception that 3.5 mg (10 μmol) of manganese (III) acetylacetonate was used instead of the manganese (II) acetate tetrahydrate. The results were a diphenyl carbonate yield of 6.0%, and by-products o- and p-bromophenol were not seen.

[0023]

Application Example 9

A reaction was carried out in the same manner as in Application Example 1, with the exception that 3.6 mg (10 μmol) of cobalt (III) acetylacetonate was used instead of cobalt (II) acetate tetrahydrate. Diphenyl carbonate was obtained at a yield of 5.5%, and by-products o- and p-bromophenol were not seen.

Translated from Japanese by the Ralph McElroy Co., Custom Division
P.O. Box 4828, Austin, Texas 78765 USA